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The Crystal and Magnetic Structures of Sr_2CoFeO_5

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The crystal and magnetic structures of the brownmillerite Sr_2CoFeO_5 have been refined from neutron powder diffraction data collected at room temperature, space group *Icmm*, a = 5.6243(2), b = 15.6515(5), c = 5.5017(2) Å. The transition metal ions are partially ordered over the 6- and 4-coordinate cation sites; in addition the 4-coordinate sites themselves have a positional disorder. The compound shows G-type antiferromagnetic order at room temperature with ordered magnetic moments of 3.2 and 2.9 μ_B, aligned along z, at the 6- and 4-coordinate sites, respectively. The low magnitude of the ordered moments is discussed.

Introduction

There are a number of compounds with the general formula $A_2B_2O_5$ which are notionally derived from the perovskite structure ABO_3 by the introduction of an ordered array of oxygen vacancies. In many compounds, for example, $Ca_2Fe_2O_5$, $Sr_2Fe_2O_5$, and $Sr_2Co_2O_5$, the vacancies order in such a way as to create a structure consisting of alternate layers of octahedrally and tetrahedrally coordinated transition metal cations; this is known as the brownmillerite structure (Fig. 1) after the mineral Ca_2FeAlO_5, itself an important constituent of Portland cement. These materials, and the mixed valence compositions ABO_{3-x} ($0 < x < 0.5$) which lie between the brownmillerite and perovskite phases, have potential as heterogeneous catalysts, and also as electrode materials.

The crystal structure of $Ca_2Fe_2O_5$ has been shown to be orthorhombic with $c < a < b$ in a space group *Pcmn* (*1*), whereas the mineral Ca_2FeAlO_5 has been shown to adopt *Ibm*2 symmetry (*2*). A neutron powder-diffraction study (*3*) indicated that $Sr_2Fe_2O_5$ has space group *Icmm*, although a subsequent single-crystal X-ray study gave the space group as *Ibm*2 (*4*). A preliminary report (*5*) has assigned the space group *Icmm* to $Sr_2Co_2O_5$. It is thus clear that although these compounds are essentially isostructural, there are subtle crystallographic differences between them. All four compounds show strong antiferromagnetic coupling between nearest-neighbor transition metal ions (G-type antiferromagnetism) at relatively high temperatures (*3, 6–8*); in the case of Ca_2FeAlO_5 the ordered component of the magnetic moment lies along the crystallographic x axis, whereas the z axis is the preferred direction in the other three compounds. In this paper we report a determination of the crystal and magnetic structures of Sr_2CoFeO_5. At

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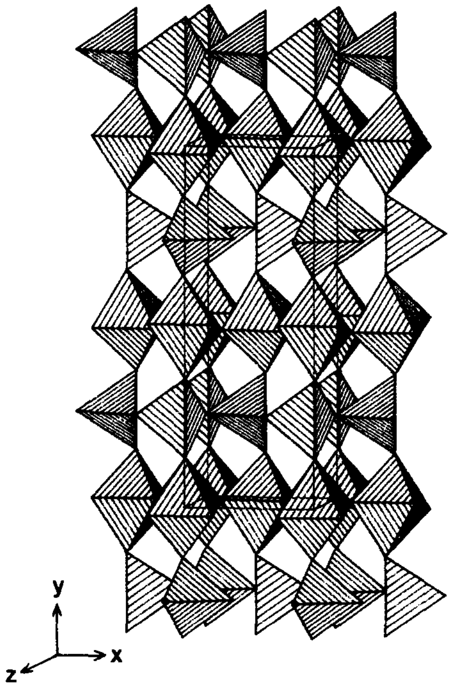

FIG. 1. The transition metal polyhedra in the brownmillerite structure.

1200°C the iron and cobalt atoms in this material are randomly distributed over the octahedral and tetrahedral sites of the brownmillerite structure (*9*). However, by annealing an aliquot under flowing argon at 800°C we were able to prepare a sample which was subsequently shown by Mössbauer spectroscopy to be antiferromagnetic at room temperature with a partial ordering of the iron and cobalt cations onto the octahedral and tetrahedral sites, respectively. The structure of this partially ordered phase is described below.

Experimental

The preparation and characterization by X-ray powder diffraction, Mössbauer spectroscopy, and magnetic susceptibility measurements of the sample used in this work have been described previously (*9*). Neutron diffraction data were collected at room temperature on a polycrystalline sample contained in a vanadium can of 12 mm diameter using the powder diffractometer D2b at ILL Grenoble. The instrument was used in the high flux mode and data were collected at 2θ intervals of 0.05° throughout the angular range $0° < 2\theta < 150°$, the experiment taking ~4 hr to complete. The mean neutron wavelength was 1.594 Å.

Results

The neutron diffraction data were analyzed by the Rietveld profile analysis method (*10*), using the following coherent scattering lengths: $b_{Sr} = 0.69$, $b_{Co} = 0.25$, $b_{Fe} = 0.95$, $b_O = 0.58 \times 10^{-12}$ cm. The background level was estimated by interpolation between regions of the profile where there were no Bragg peaks, and statistical variations in the background level were taken into account in assigning a weight to each profile point. Data with $2\theta < 32°$ were excluded from the analysis because of highly asymmetric peak shapes. Simultaneous refinement of the crystal and magnetic structures was attempted in the (crystal) space groups *Pcmn*, *Ibm*2, and *Icmm*, with the magnetic moment of the cations constrained to lie along one of the crystallographic axes in a G-type magnetic structure. The best agreement between the observed and calculated diffraction patterns was achieved when the magnetic moments were constrained to lie along *z*, with the crystal structure adopting space group *Icmm*. The final weighted profile *R*-factor was then 13.05%, with Bragg and magnetic *R*-factors of 6.06 and 13.22% respectively. The observed, calculated, and difference profiles are drawn in Fig. 2, and the refined values of the structural parameters are listed in Table I. Selected bond distances and bond angles are presented in Table II. The average magnetic moments of the octahedral (Co/Fe1) and tetrahedral (Co/Fe2)-

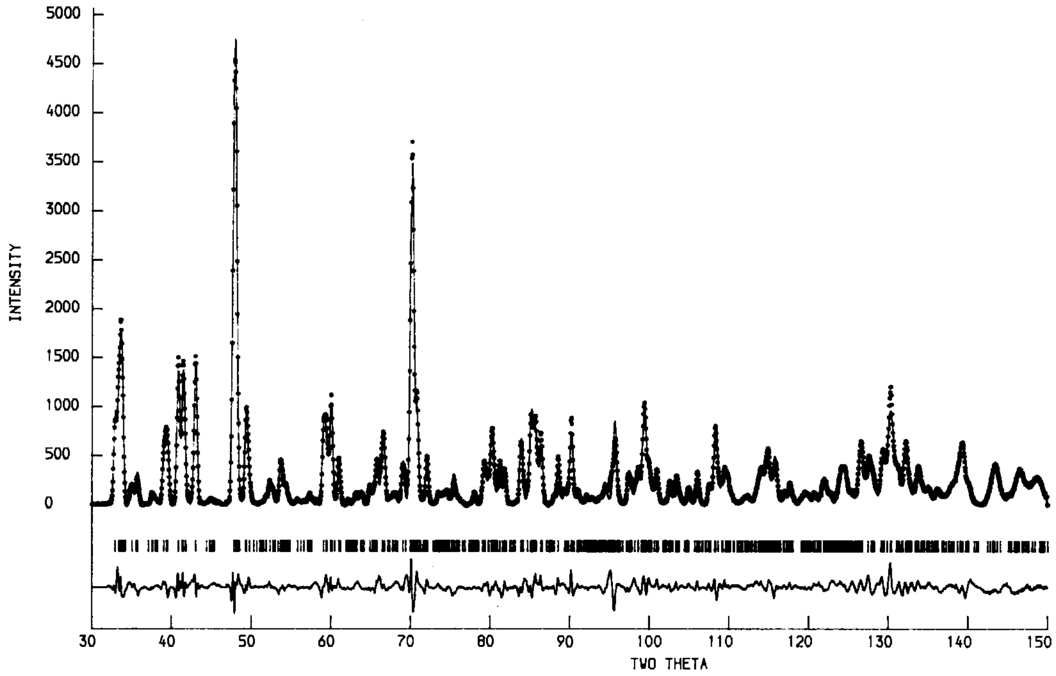

FIG. 2. Observed (···), calculated (—), and difference profiles for Sr_2CoFeO_5 at room temperature. Reflection positions are marked.

site cations refined to values of 3.2(1) and 2.9(1) μ_B, respectively when the Co^{3+} free-ion form factor calculated by Watson and Freeman (*11*) was used to describe the 2θ-dependence of the magnetic scattering length. However, this is most unlikely to be an adequate form factor, because it makes no allowance for the orbital component of the magnetic moment of high-spin $Co^{3+}: 3d^6$, which would be expected to expand the form factor. Furthermore, we are using one form factor, that calculated for Co^{3+}, to describe the average scattering from two species, Co^{3+} and Fe^{3+}, and the form factor of the larger Fe^{3+} ion will be contracted relative to that of Co^{3+}. The validity of our chosen form factor is thus extremely doubtful, and we therefore attempted to adjust the form factor empirically in order to obtain the best agreement between the observed and calculated diffraction patterns. The agreement factor proved to be rather insensitive to the exact shape of the form factor used, any attempt to expand the form factor being compen-

TABLE I

STRUCTURAL PARAMETERS FOR Sr_2CoFeO_5 AT ROOM TEMPERATURE

Atom	Site	*x*	*y*	*z*	*B* (Å²)
Sr	8h	0.0112(4)	0.1101(1)	$\frac{1}{2}$	0.51(3)
Co/Fe1[a]	4a	0	0	0	0.29(4)
Co/Fe2[b]	8i	0.9335(6)	$\frac{1}{4}$	0.0391(8)	0.29(4)
O1	8g	$\frac{1}{4}$	0.9940(2)	$\frac{1}{4}$	0.49(3)
O2	8h	0.0443(4)	0.1409(2)	0	0.91(4)
O3	8i	0.8669(9)	$\frac{1}{4}$	0.6260(0)	0.71(8)

Note. Space group *Icmm*, $a = 5.6243(2)$, $b = 15.6515(5)$, $c = 5.5017(2)$ Å.

[a] 56.7% Fe, 43.3% Co (±1%).

[b] 56.7% Co, 43.3% Fe.

The 8i sites are only half occupied.

TABLE II

BOND LENGTHS (IN Å) AND BOND ANGLES (IN DEGREES) FOR Sr_2CoFeO_5 AT ROOM TEMPERATURE

Octahedral site			Tetrahedral site		
Co/Fe1–O1	1.969(3)	×4	Co/Fe2–O2	1.831(7)	×2
Co/Fe1–O2	2.219(4)	×2	Co/Fe2–O3	1.880(9)	
				1.918(9)	
O1–Co/Fe1–O1	91.39		O2–Co/Fe2–O2	138	
O2–Co/Fe1–O1	91.87		O3–Co/Fe2–O2	104	
			O3–Co/Fe2–O2	101	
			O3–Co/Fe2–O3	107	
O1–O1	2.818(4)	×2	O2–O2	3.415(5)	
O1–O1	2.751(4)	×2	O2–O3	2.958(8)	
O1–O2	2.918(5)	×2	O2–O3	2.854(8)	
O1–O2	3.014(5)	×2	O3–O3	3.05(1)	
Sr site					
Sr–O1	2.645(4)	×2	Sr–O2	2.799(4)	×2
	2.589(4)	×2		3.161(4)	
				2.546(4)	
Sr–O3	2.437(8)	×2			

sated for by a reduction in the refined value of the magnetic moment and vice versa, an effect which reflects the relatively small proportion of magnetic scattering in the diffraction pattern. Thus, although we have established that G-type antiferromagnetism is present in Sr_2CoFeO_5 at room temperature, we would not claim to have determined the average value of the ordered component of the magnetic moments at the octahedral and tetrahedral sites to better than 15% accuracy.

Discussion

The structure described above for Sr_2CoFeO_5 is very similar to that reported by Greaves *et al.* (*3*) for $Sr_2Fe_2O_5$. The relatively high value of the weighted profile R-factor is partly due to the presence of a large number of weak peaks in the diffraction pattern. The material is perovskite based, with alternate layers of 6- and 4-coordinated transition metal cations along the y axis (see Fig. 1), a consequence of anion vacancy ordering in the compound $SrCo_{0.5}Fe_{0.5}O_{2.5}$. The coordination geometry at the 6-coordinate site is reasonably close to regular octahedral, although there is a pseudotetragonal elongation along the y axis. The geometry at the 4-coordinate site, although conveniently referred to as tetrahedral, is quite irregular as demonstrated by the bond angles and lengths in Table II. The use of the space group *Icmm* requires statistical disorder of both the 4-coordinate cations and the oxygen atom O3 over two sets of equivalent sites, i.e., by half-occupation of the 8i sites. Note that O3 has only 4-coordinate cations as neighbors, whereas O1 has only 6-coordinate cation neighbors; O2 provides the link between the octahedral and tetrahedral layers. The metal–oxygen bond distances at the 4-coordinate site are smaller than those about the 6-coordinate site, as is to be expected.

The disorder onto the 8i sites in *Icmm* is identical to the structure reported by Greaves *et al.* (*3*) for $Sr_2Fe_2O_5$; they also suggest that the structure contains short-range order over a few unit cells in the space group *Ibm*2 as adopted by Ca_2FeAlO_5, but do not attempt to explain it. In the brownmillerite structure the relative orientation of the equivalent tetrahedra alternate along y so that the layer sequence can be written as OTOT′OTOT′ . . . , and the b parameter is four times the perovskite cubic cell parameter ($4a_c$). Other "intergrowths" of the perovskite and brownmillerite structural types are known. The oxide $Ca_2LaFe_3O_8$ contains pairs of octahedral-site layers separated by tetrahedral-site layers. Electron diffraction data give some evidence (*13*) to suggest that two polymorphs with the layer sequences OOT . . . ($3a_c$) OOTOOT′ . . . . ($6a_c$) can occur. Another sequence OTOOTOT′OOT . . . ($10a_c$) has been proposed (*14*) for $Ca_4YFe_5O_{13}$. Bearing these examples in mind, it seems logical that an incorrect stacking sequence could occur at intervals along y in the brownmillerite structure which would be seen in the diffraction data as a positional disorder of the tetrahedral sites. This would also explain the observation (*4*) of a different space group for single-crystal $Sr_2Fe_2O_5$, where the better crystallinity could result in fewer faults in the stacking sequence.

The extent of the cation ordering over the octahedral and tetrahedral sites (57/43—see Table I) is comparable to that found in our earlier Mössbauer study (62/38). The small discrepancy between the two values may reflect a difference in the recoilless fraction at the two sites, which was not taken into account in the spectroscopic measurement.

The ordered magnetic moments on the transition metal cations appear to be rather low, even if allowance is made for incomplete saturation at room temperature and a possible contraction of the form factor. The Mössbauer data and the observation of a low moment on the tetrahedral site allow us to discount the presence of diamagnetic low-spin Co^{3+} as a source of the anomaly. The ordered moment of a high-spin $Fe^{3+}:3d^5$ ion would normally be ~4.4 μ_B, and a value of >4 μ_B would also be expected for a high-spin $Co^{3+}:3d^6$ on an octahedral site. The amount of Fe^{3+} would be little changed on moving to a tetrahedral site although that of Co^{3+} would be lowered as the contribution of the orbital component is reduced. However, it is unlikely that the average tetrahedral moment would drop below 3.8 μ_B in this structure, and it is barely possible to rationalize the observed values without suggesting that the long-range magnetic order may be perturbed by the disorder on the tetrahedral sites.

It is interesting to note that the disordered isostructural compounds $Sr_2Fe_2O_5$ and $Sr_2Co_2O_5$ (*3*, *8*) also have relatively low magnetic moments (4.0 ± 0.1 and 3.3 ± 0.5 μ_B) associated with the cations sites, whereas the ordered compound $Ca_2Fe_2O_5$ (*6*) has the expected moment of 4.5 ± 0.2 μ_B per Fe^{3+} ion.

A refinement using a 10% contraction in the form factor only increased the values of the moments at the octahedral and tetrahedral sites to 3.7 and 3.3 μ_B, respectively. The values of the hyperfine field observed by Mössbauer spectroscopy (*9*) indicate a degree of saturation close to 90% at room temperature. It is thus difficult to imagine a saturation moment of greater than 4.1 μ_B on the octahedral site and 3.6 μ_B on the tetrahedral site, both values still being lower than those which might have been expected.

The saturated internal hyperfine field determined by Mössbauer spectroscopy is similar in $Ca_2Fe_2O_5$, $Sr_2Fe_2O_5$, $Sr_2Co_2O_5$, and Sr_2CoFeO_5, thus implying that the local magnetic order is complete, even in the disordered materials. The structural disorder only appears to perturb the magnetic moment over the larger distances (~200 Å) sampled in a diffraction experiment. The fact that the spins order along x in Ca_2FeAlO_5 (*7*) leads to a possible rationalization of these observations, because it suggests that the energy difference between spin systems aligned along x and z is small. It is therefore quite reasonable to postulate that each spin in the disordered materials can have a component along both x and z, but that only those components along z show long-range ordering. This is consistent with the orthorhombic symmetry of the crystal structure, whereas an ordering of both components would imply monoclinic symmetry. Our model is also consistent with the Mössbauer spectra (*9*) which record the full, local hyperfine field and not just that component showing long-range order. The magnetic dipole and electric quadrupole hyperfine interactions in both $Ca_2Fe_2O_5$ and Ca_2FeAlO_5 have been exhaustively studied (*15*). The principle value of the electric field gradient lies along y at the tetrahedral sites and close to y at the octahedral sites, with only small values of the asymmetry parameter in both cases. This has the result that the spin directions (along z in $Ca_2Fe_2O_5$, along x in Ca_2FeAlO_5) are always perpendicular (or nearly so) to the principal axis of the electric field gradient. As a result the Mössbauer hyperfine patterns for the two compounds are almost identical despite the change of spin-axis. Thus, in the present instance of Sr_2CoFeO_5 the Mössbauer spectrum on powdered samples will be very insensitive to any variation in the spin directions within the xz plane. Although the experimental linewidths are broader than in $Ca_2Fe_2O_5$ and $Sr_2Fe_2O_5$, this could equally be due to small local fluctuations in the electric field gradient produced by the cation disorder.

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